Chapter 9
Continuously Operated Cooligomerisation of Fatty Compounds with Ethylene

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9.1 Introduction

Branched fatty derivatives are particularly used in lubricant industry. Branched fatty derivatives have at least one branching point in the alkyl group resulting in a change of the three-dimensional structure which leads to a molecular angling [1]. Due to this angling of the carbon chain, the branched derivatives can be clearly distinguished from the linear homologs in their physical properties [2–5].

The huge commercial potential, particularly in cosmetics and lubricants industry, is based on the following typical properties of branched fatty derivatives [6, 7]:

- Low melting point
- High thermal and oxidative stability
- Low viscosity
- Low surface tension
- High wettability (spreadability)
- High solubility of the corresponding salts in aqueous and organic solutions
- Low packing density
- High water vapour permeability.

The low melting point allows the application in refrigeration as well as in high temperature technology. Branched fatty derivatives are stable and liquid over a wide temperature range and their low viscosity and surface tension lead to good lubricant properties [7].

The high solubility and wettability result in a higher hydrophilie and give commercial potential in the cosmetics industry. Due to the low packing density caused by the branched carbon chain, the crèmes, lotions, and deodorants have high water vapour permeabilities. Concurrently, the high chemical stability ensures the required colour and odour stability [8, 9]. The high spreadability leads to a low critical micelle concentration, which allows the application as detergents additives, or in the production of surfactants. Because of the high solubility of the corresponding salts, they

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can be additionally used as drying agents for paints and coatings, for the extraction of metals, for corrosion protection, and as additives in polymers.

9.1.1 Cooligomerisation of Fatty Compounds with Ethylene

Branched fatty derivatives are industrially produced as side products of fatty acid dimerisation or "Guerbetisierung" of fatty alcohols [10–12]. Further ways for the synthesis of branched fatty derivatives are described among others from Metzger et al. [13], Foglia et al. [14] and Behr et al. [15].

An alternative process for the production of branched fatty derivatives is the cooligomerisation of diunsaturated fatty compounds such as conjugated linoleic acid or methyl linoleate, which has already been investigated in laboratory scale [16–21].

Within those investigations, the direct formation of the branched derivatives from linoleic acid or methyl linoleate with ethylene was investigated (Fig. 9.1). The reaction scheme shows a tandem reaction consisting of the conjugation of methyl linoleate to methyl conjugate followed by the cooligomerisation of methyl conjugate with ethylene to the branched fatty derivatives.

This route leads directly from industrially easily accessible basic oleochemicals (linoleic acid technical: 62.0 w-% or methyl linoleate technical: 59.3 w-%) to the designated product.

The cooligomerisation was investigated with linoleic acid [21] as well as with methyl linoleate [22] like it is described in the following chapters. The examination of reaction conditions and achieved yields showed no significant differences between the different oleochemical educts.

9.2 Batch Investigations

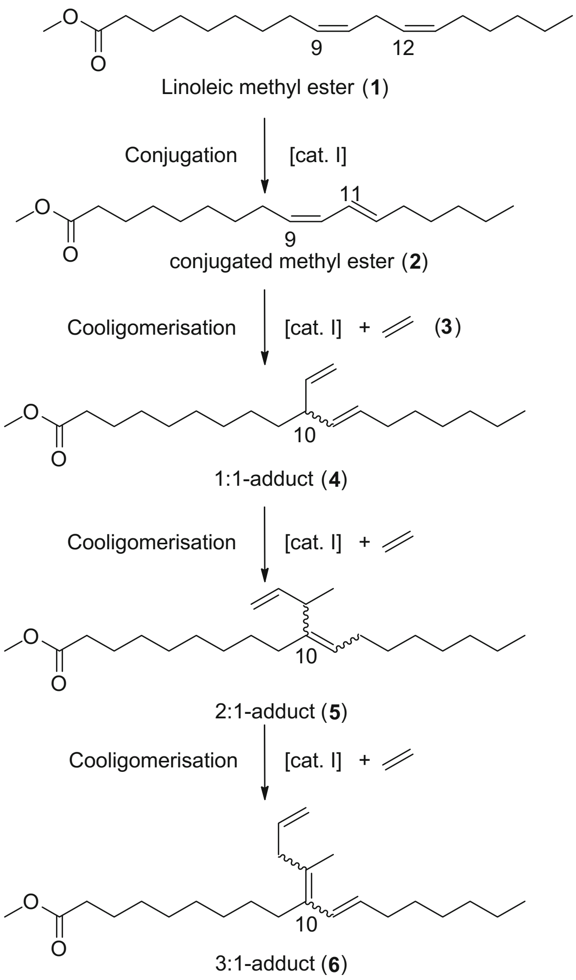
9.2.1 Conjugation and Cooligomerisation in Laboratory Scale

The tandem reaction consisting of conjugation and cooligomerisation requires a catalyst, which favours both reactions. Within the investigations of the isolated conjugation, highly active as well as moderately active homogenous catalysts could be found [9]. Concerning the tandem reaction, only $RhCl_3 \cdot 3H_2O$ appeared as a promising homogenous precursor. This precursor has already been successfully used for conjugation with ethylene in investigations of Behr and Laufenberg [16], Behr and Fängewisch [19], Behr and Miao [20], and Behr et al. [21].

While the catalyst based on the $RhCl_3 \cdot 3H_2O$ precursor is only moderately active regarding the isolated conjugation, it is highly active for the cooligomerisation so that the chemical equilibrium is shifted in favour of the branched products.

Additionally to the precursor $RhCl_3 \cdot 3H_2O$, in which the active rhodium species has the oxidation state III, a regeneration additive in form of an alkyl halides is

Fig. 9.1 Tandem reaction of methyl linoleate and ethylene forming branched fatty derivatives



needed. The addition of an alkyl halide like crotyl chloride is necessary for the reoxidation of the inactive Rh(I)-species, which appears during the catalyst cycle. At optimised reaction conditions, the achievable yield of branched derivatives via tandem reaction is around 92% (Fig. 9.2). The formation of the product is consecutive: At first the methyl conjugate is formed, secondly one molecule of ethylene is added to form the 1:1 derivative **4**. Before the next molecule of ethylene can be added, a conjugation has to occur once again so that the 2:1 derivative **5** can be formed. Higher branched products than the 3:1 derivate **6** have not been detected.

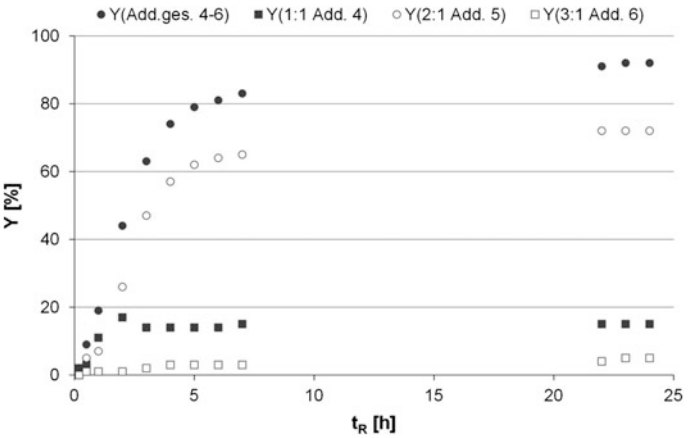


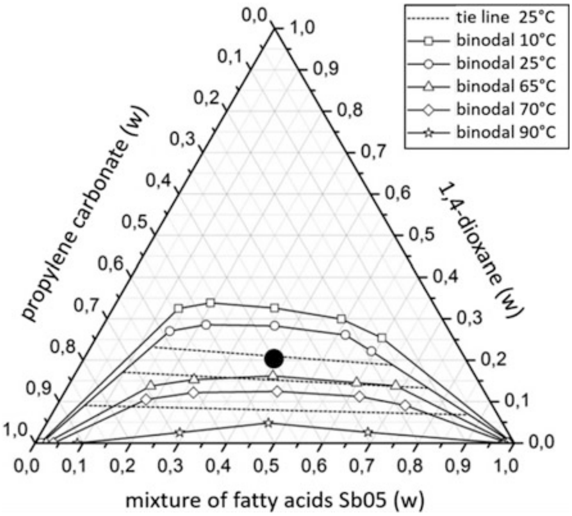
Fig. 9.2 Yield time curve for the production of branched fatty derivatives [21]. Reaction conditions: *Cat.* $RhCl_3{\cdot}3H_2O$; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{\text{1,4-Dioxane}} = 0.2$; $c_{\text{cat.}} = 1$ mol%; $n_{\text{Reg}}/n_{\text{Kat}} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

9.2.2 Catalyst Recycling

To recycle the catalyst, a thermomorphic multicomponent solvent (TMS) system is used. The TMS consists of the polar component propylene carbonate, the medium polar solvent 1,4-dioxane, and the non-polar fatty compounds. The ternary diagram in Fig. 9.3 illustrates the liquid–liquid equilibrium of this mixture [21].

At room temperature and below the indicated operating point ($w_{\text{propylene carbonate}} = 0.4$, $w_{\text{Emery,SB05}} = 0.4$ and $w_{\text{1,4–dioxane}} = 0.2$) is a two-phase mixture so that

Fig. 9.3 Ternary diagram for propylene carbonate, 1,4-dioxane and fatty compounds (Emery Oleochemicals Edenor SB05) *filled circle* operating point [21]



the catalyst recycling can be easily realised by separation of the liquid phases. At a reaction temperature of 70 °C, the mixture consists of only one liquid phase which is very important to control the considered reaction. In case of a gas–liquid–liquid reaction system, the cooligomerisation is highly limited by mass transfer which is indicated by a critical reduction in yield.

9.2.3 Catalyst Leaching

Using the described TMS-system, the catalyst leaching was higher than it was anticipated. That is why the cause for a high loss of the catalyst into the product phase was investigated, initially.

Propylene carbonate solvated the homogenous rhodium catalyst complex without prior heating. With prior heating up to reaction temperature, the catalyst leaching is rising enormously. At reaction temperature, the catalyst complex is strongly coordinating to the double bonds of the oleochemicals. Even after cooling the solution down this bonding does not get detached (Fig. 9.4).

The amount of catalyst leaching depends on the type and number of double bonds: conjugated double bond, unconjugated double bond, single double bond, no double bond. The functional group of the molecule does not effect the leaching, so that the results of methyl stearate and n-hexane do not differ.

9.2.4 Application of Ligands

To minimise the strong coordination of the catalyst complex to the fatty compounds the application of ligands is possible. However, it was shown that a minimised catalyst leaching is always combined with a decrease in yield. The only ligand

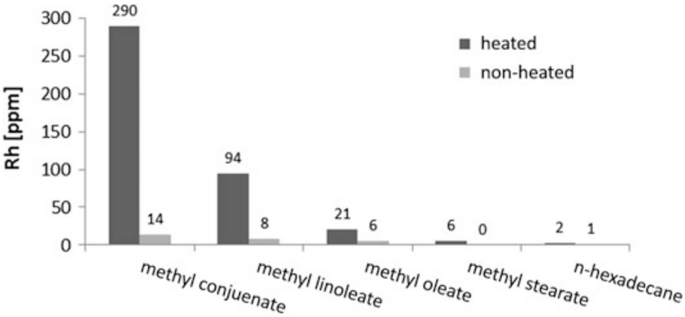


Fig. 9.4 Examination of the solubility behaviour of the catalyst with different unpolar components in two-phase mixtures with and without prior heating [22]. Conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Solvent* Propylene carbonate; $w_{\text{unpol.comp.}} = 0.5$; $c_{\text{cat.}} = 0.5$ mol%; $t = 5$ h; $T = 70$ °C; $T_{\text{Separation}} = -5$ °C, RT with methyl stearate)

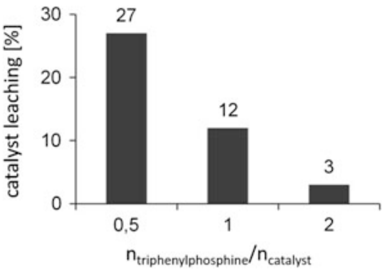


Fig. 9.5 Influence of the triphenylphosphine to catalyst ratio to the catalyst leaching into the product phase. conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Ligand* Triphenylphosphine; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{1,4\text{-Dioxane}} = 0.2$; $c_{\text{cat.}} = 1$ mol%; $n_{\text{Reg}}/n_{\text{Kat.}} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

which minimises the catalyst leaching in an acceptable manner and still allows moderate conjugation and cooligomerisation is triphenylphosphine [23, 24].

The concentration of the ligand influences the achievable leaching and yield. In general the more ligand is used the lower the leaching and the yield is (Figs. 9.1 and 9.5). An increasing concentration of the ligand leads to a suppressed coordination of the ligand to the fatty compounds. But this effect is simultaneously combined with a suppressed tandem reaction which leads to a loss in yield (Fig. 9.5).

Figure 9.6 shows the yield time curve with different triphenylphosphine (TPP) concentrations. Higher concentrations lead to a suppressed tandem reaction so that a compromise between minimised leaching and moderate yield has to be found. Initially, the recycle of the catalyst has to be proven in continuous operation so it is reasonable to use a ligand concentration of 2 mol%.

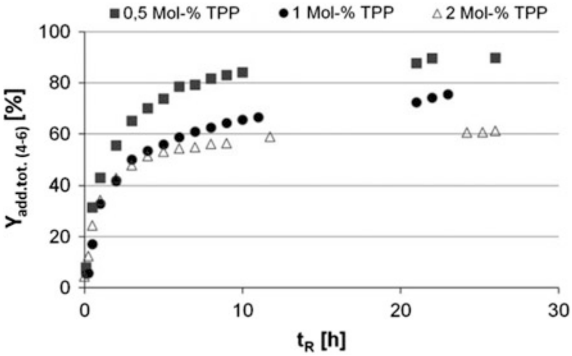


Fig. 9.6 Triphenylphosphine influence to the tandem reaction of cooligomerisation and conjugation of linoleic acid with ethylene [20, 21]. conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Ligand* Triphenylphosphine TPP; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{1,4\text{-Dioxane}} = 0.2$; $c_{\text{cat.}} = 1$ Mol-%; $n_{\text{Reg}}/n_{\text{Kat.}} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

9.3 Miniplant Investigations

9.3.1 Miniplant Concept for Continuous Operation

Based on laboratory investigations, Witte [21] designed a miniplant concept, which is shown in Fig. 9.7 (block flow chart) and in Fig. 9.8 (process flow chart).

The fatty compounds are dosed together with the solvent dioxane and propylene carbonate from the storage vessel B-01 to the continuous stirred tank reactor (CSTR) B-02 using a piston diaphragm pump P-01 (Fig. 9.9). The loss of solvent according to the ternary diagram in Fig. 9.3 is compensated by continuous dosing so that a constant composition is guaranteed. The continuous pressure of 10 bar is provided by using a pressure reducer. In the separator B-03, the separation of the two phases takes place at 10 °C and 10 bar. CSTR and separator are operated at the same pressure so that the recycle of the catalyst containing polar phase and the recycle of the gas phase can be easily realised.

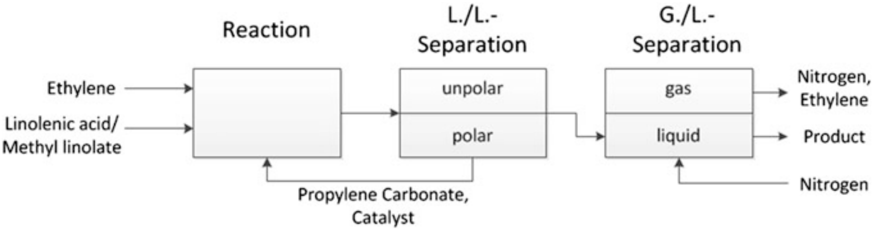


Fig. 9.7 Block flow chart of the designed miniplant for continuous production of branched fatty derivatives

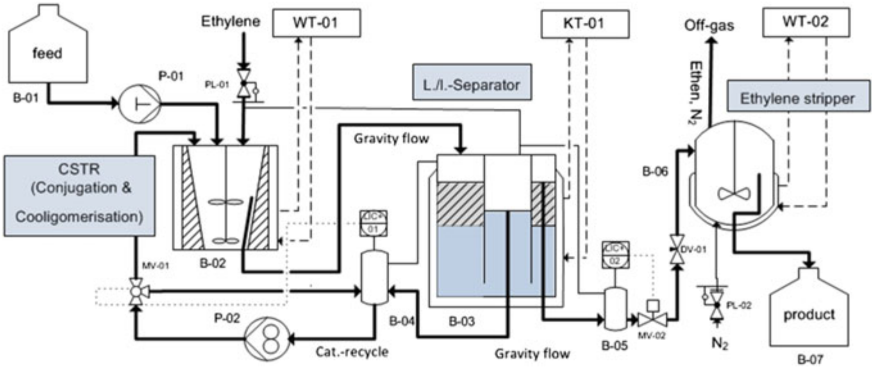


Fig. 9.8 Process flow chart of the designed miniplant for continuous production of branched fatty derivatives [22]

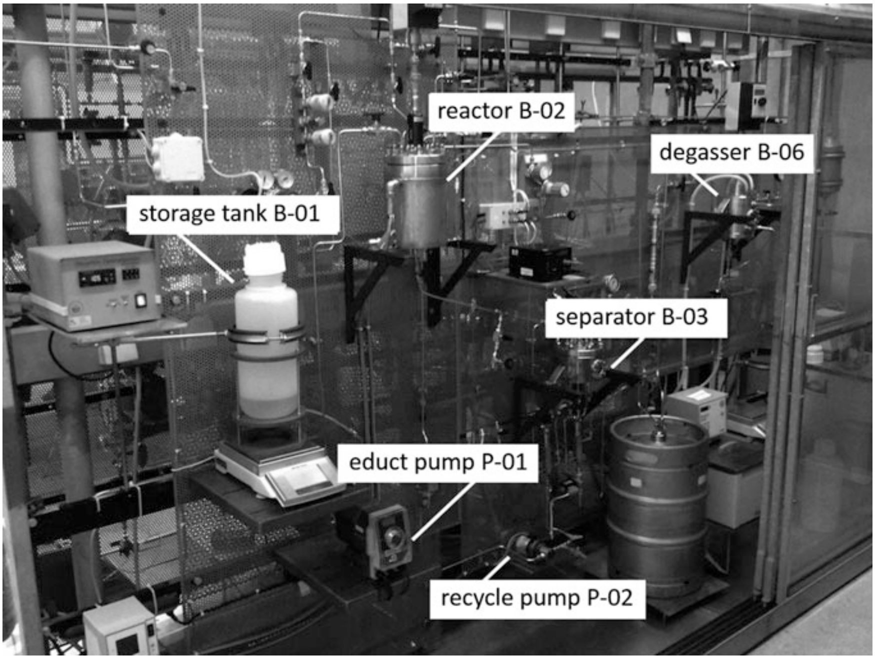


Fig. 9.9 Miniplant for the continuous production of branched fatty

By means of a gear pump P-02, the polar catalyst phase is recycled from the separator back to the CSTR. The unpolar product phase flows pressure controlled from the separator to the stripper B-06 and is expanded to atmospheric pressure. In the stripper, a continuous nitrogen stream removes remaining ethylene at 60 °C. Gravity driven the product phase flows to the product vessel B-07.

The designed, built, and tested miniplant for the continuous production of branched fatty derivatives at the chair of Technical Chemistry is shown in Fig. 9.9.

9.3.2 Miniplant Equipment

9.3.2.1 Vessels

The CSTR B-02 was designed and is based on the shape of a truncated cone with a Volume of approximately 820 ml.

Due to the geometry of the CSTR (Fig. 9.10) high retention times combined with low flow rates are possible. The truncated cone geometry allows small filling volume but still high filling level so that the required mixing of the liquid phase is provided. It is possible to use one or more angled turbine blades depending on the filling level. The respective stirrer blades of the different stirrers are designed for the referring reactor diameters at different filling levels.

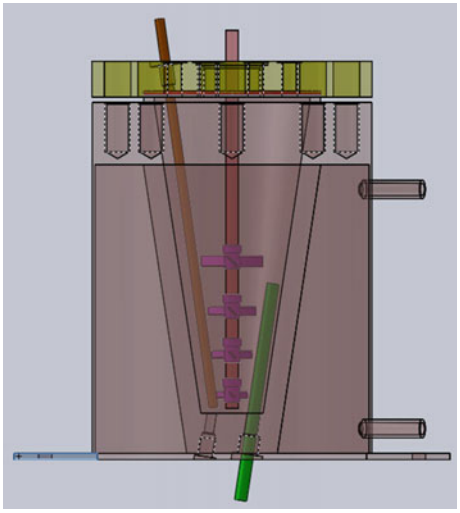


Fig. 9.10 Cross section of the designed CSTR with truncated cone geometry [21]

Separator B-03 and stripper B-06 both are built with cylindrical geometry and can be heated by a double shell like the CSTR. The operating principle of the separator was invented like it is shown in Fig. 9.11. The integrated inner tube in separator B-03 is attached to the vessel lid. The liquid stream from the CSTR flows into the outer area in the separator. The heavy phase gets into the inner tube through a gap at the bottom of the vessel. Due to the density differences the specific heights h1, h2, h3 are adjusted. Through the corresponding risers the phases leave the separator gravity controlled.

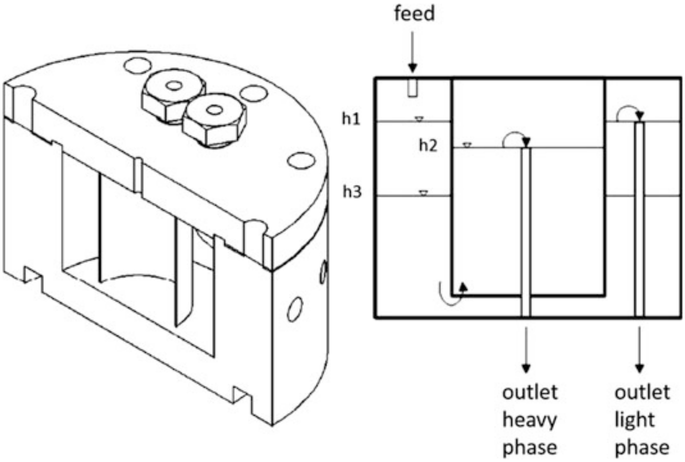


Fig. 9.11 Operating principle of the used separator B-03: The separation of the two phases is realised by the density differences

The acquisition and control of the pumps and thermostats is realised by using the software National Instruments LabView® combined with the hardware interface National Instruments CompactRIO®. The control of the solenoid valves MV-01 and MV-02 (see Fig. 9.8) for the catalyst recycle and the expansion of the product phase is deliberately decoupled from the LabView control system. Those valves are controlled autonomously by an electronic transistor circuit so that it is possible to operate the whole miniplant in continuous manner without using the control system.

9.3.3 Miniplant Operation in Continuous Manner

The optimised reaction conditions from laboratory investigations under continuous pressure can be transferred to the miniplant. To start up, the reactor is run for five hours in batch operation while in continuous operation the retention time is set to 2 h.

The yield time curve is shown in Fig. 9.12 for a continuous 100 h operation. The switch from batch to continuous operation was realised after five hours while a decrease in yield of about 10% is the response. Afterwards the reaction is levelling off in between 22 and 25%.

The stationary plateau indicates that the catalyst was effectively recycled while continuous operation. The catalyst leaching of 2% matches the investigations in laboratory scale.

The recyclability was proven in continuous operation in miniplant, but with the achieved yield of maximum 25% and a catalyst leaching of 2% the process is not

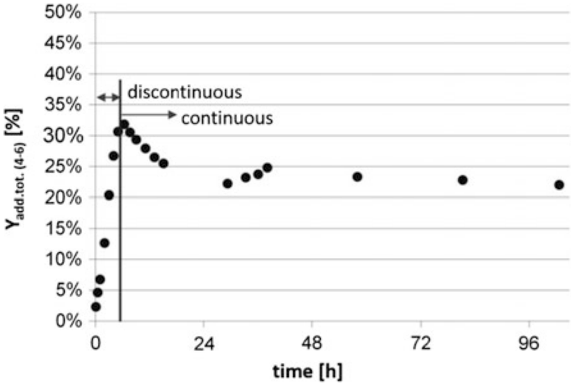


Fig. 9.12 Yield time curve of a miniplant operation for the production of branched fatty derivatives (reactor retention time 20 h). Conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Ligand* Triphenylphosphine; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and propylene carbonate; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{1,4\text{-Dioxane}} = 0.2$; $c_{\text{cat.}} = 1$ mol%; $c_{\text{TPP.}} = 2$ mol%; $n_{\text{Reg}}/n_{\text{Kat.}} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

economically reasonable. Higher yields can only be achieved by using no ligands which on the other hand leads to a higher catalyst leaching.

Therefore, a process with alternative catalyst recycling was investigated. Like it is shown in Fig. 9.4 the homogeneous catalyst coordinates to the unsaturated compounds. So it is presumed that the coordination will be detached after hydrogenation of the unsaturated, branched, fatty derivatives. Investigations have shown that the rhodium catalyst can be gained back from the saturated, branched, fatty derivatives (Iodine Value = 10) using propylene carbonate as extraction agent. Under optimised conditions, the rhodium leaching can be minimised from 450 ppm (after cooligomerisation without using ligands) to 4 ppm ($m_{\mathrm{PC}}/m_{\text{product mixture from cooligomerisation}} = 1/10$, $T_{\mathrm{Extr.}} = 25$ °C, 4-stage sequential extraction).

9.3.4 Hydrogenation

For the hydrogenation of the branched fatty derivatives, a heterogeneous palladium on activated carbon (1%) catalyst has been found to be most active. The most reasonable solvent concerning achieved iodine value, price, and boiling point is methanol. For the optimisation of pressure and temperature, the rhodium adsorption to the heterogeneous catalyst is from great interest.

Figures 9.13 and 9.14 show the Rhodium concentration of the product phase after hydrogenation as a function of pressure and temperature. The lower the pressure and temperature are, the higher the Rhodium content in the product mixture is after hydrogenation. According to the results, the rhodium adsorption is strongly depending on the preset pressure and temperature, so in miniplant scale it is reasonable to operate with low pressure and low temperature. Further experiments show that the pressure has a slight effect on iodine value, while 5 and 10 bar lead to slightly lower iodine values there was no difference found between 20 and 50 bar (Iodine value = 35). The temperature dependence is almost negligible, so that after one hour there is no difference between iodine values for hydrogenation at temperatures between 25 and 90 °C.

9.3.5 Optimised Miniplant Concept

Figure 9.15 illustrate the flow chart of the optimised process for the production of the saturated, branched, fatty derivatives and Fig. 9.16 shows the corresponding process flow chart.

The product mixture from the cooligomerisation process is mixed with methanol in a buffer tank (B-07) and then dosed to the trickle bed reactor consisting of tree sequential tubular reactors (B-08). The saturated mixture is then expanded to atmospheric pressure and in the stripper B-09 a continuous nitrogen stream removes remaining hydrogen. The next step is the distillation (B-11) to separate and recycle

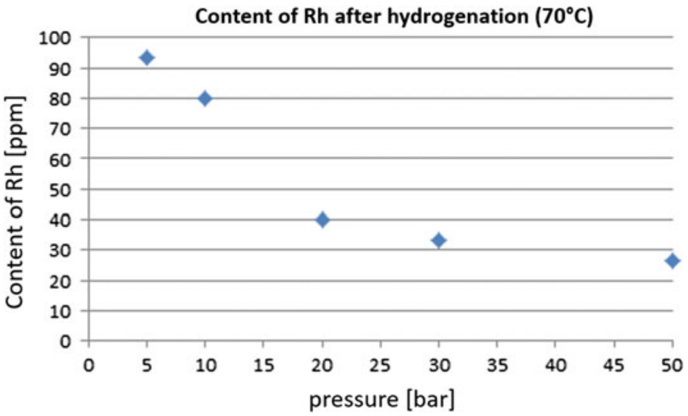


Fig. 9.13 Rhodium content in the product mixture after hydrogenation in function of the pressure. Conditions: *Hydrogenation* Pd/C 1%; *Solvent* Methanol; T_R = 70 °C; 100 rpm, m_{Cat} = 1 g, conti pressure *Conditions* cooligomerisation.: *Cat.* $RhCl_3$ $3H_2O$; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* methyl linoleate (w-% of methyl linoleate in educt $w_{\mathrm{methyl\ linoleate}} = 0.59$); $w_{\mathrm{methyl\ linoleate}} = 0.4$; $w_{\mathrm{Propylene\ Carbonate}} = 0.4$; $w_{1,4\text{-}\mathrm{Dioxane}} = 0.2$ $c_{\mathrm{cat.}} = 1$ mol%; $n_{\mathrm{Reg}}/n_{\mathrm{Cat.}} = 25$; T_R = 70 °C; p_{Ethylene} = 10 bar contin; 750 rpm, $T_{\mathrm{Separation}}$ = 10 °C, L_{Rh} = 450 ppm

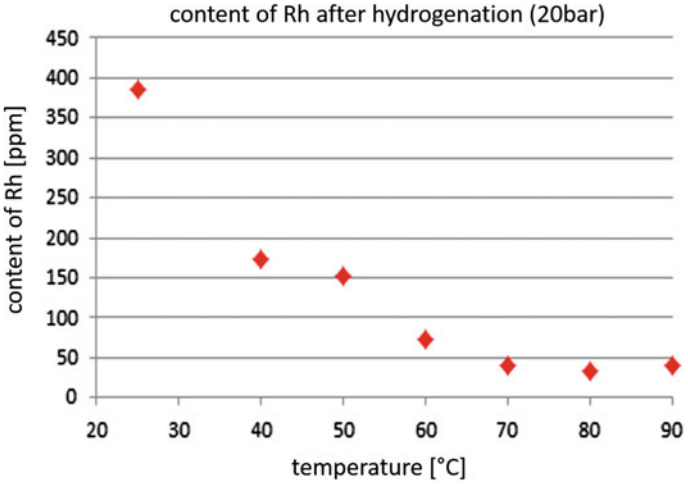


Fig. 9.14 Rhodium content in the product mixture after hydrogenation in function of the temperature [22]. Conditions: *Hydrogenation* Pd/C 1%; *Solvent* Methanol; p_{H2} = 20 bar conti; 100 rpm, m_{Cat} = 1 g, *Conditions* cooligomerisation.: *Cat.* $RhCl_3$ $3H_2O$; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* methyl linoleate (w-% of methyl linoleate in educt $w_{\mathrm{methyl\ linoleate}} = 0.59$); $w_{\mathrm{methyl\ linoleate}} = 0.4$; $w_{\mathrm{Propylene\ Carbonate}} = 0.4$; $w_{1,4\text{-}\mathrm{Dioxane}} = 0.2$ $c_{\mathrm{cat.}} = 1$ mol%; $n_{\mathrm{Reg}}/n_{\mathrm{Cat.}} = 25$; T_R = 70 °C; p_{Ethylene} = 10 bar contin; 750 rpm, $T_{\mathrm{Separation}}$ = 10 °C, L_{Rh} = 450 ppm

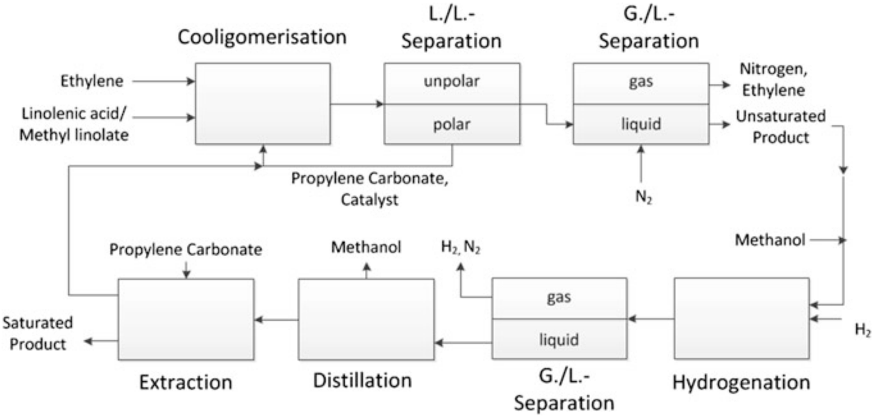


Fig. 9.15 Flow Chart of the optimised process for the production of saturated, branched, fatty derivatives

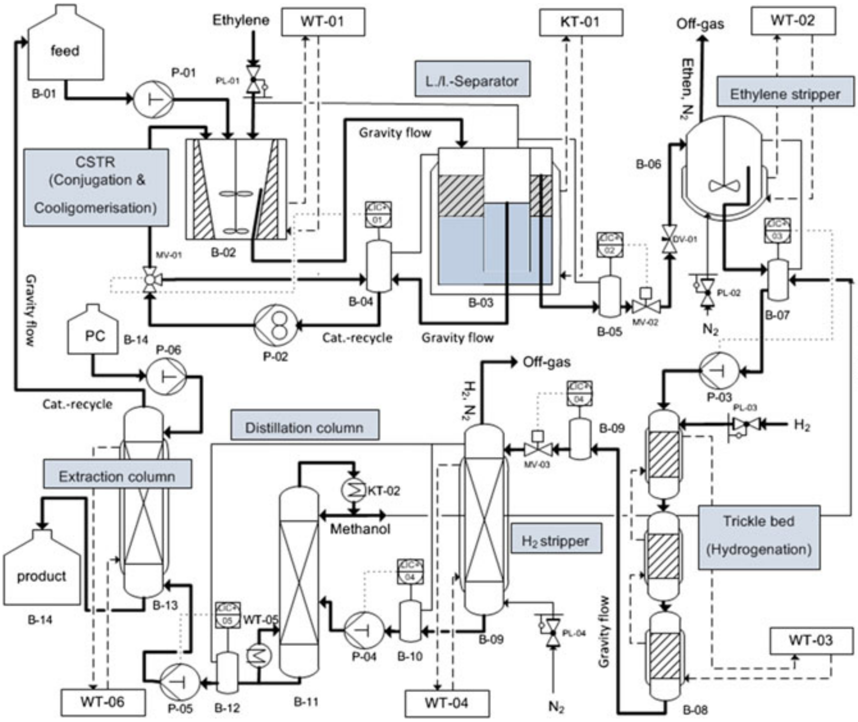


Fig. 9.16 Process flow chart of the designed miniplant for the optimised continuous production of branched fatty derivatives

the methanol used for the hydrogenation step. After separating the mixture from methanol the last unit is the extraction of the remaining homogeneous rhodium catalyst using propylene carbonate as extracting agent. The extracted catalyst recycle can then be dosed to the feed storage. The additional propylene carbonate is supposed to compensate the solvent loss in the liquid–liquid separator (B-03).

The hydrogenation step was studied in detail. While palladium catalyst is able to hydrogenate the branched unsaturated products **4-6**, the leached rhodium from the homogeneous catalysed cooligomerisation is precipitated on the surface of the heterogeneous catalyst. This indicates that the product quality is not suffering from rhodium loadings any further. The trickle bed was operated for 100 h and showed a stable behaviour. A rhodium doped catalyst was found after this experiment.

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